Acidity of conventional luting cements and their diffusion through bovine dentine

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Abstract

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Aim To examine the changes in pH of luting cements and acid diffusion of luting cements through bovine dentine using a pH-imaging microscope (SCHEM-100; Horiba Ltd, Kyoto, Japan).

Methodology The pH of the surface of three conventional luting cements, glass-ionomer, zinc phosphate and zinc polycarboxylate was measured with SCHEM-100 for 1 month. The acid diffusion from the three luting cements through bovine dentine was investigated by measuring pH changes during the application of each luting cement on the bovine dentine surface. Coronal bovine dentine disks were prepared to thicknesses of 0.50 and 0.25 mm. Each luting cement was placed on the labial dentine surface, and the pH change of the pulpal surface was observed every 3 min for 30 min with SCHEM-100.

Results Glass-ionomer showed the lowest pH values for longer times. Neutralization proceeded furthest in zinc polycarboxylate. The 0.5-mm-thick dentine disks showed no pH change on the pulpal side with all the three cements. The 0.25-mm-thick disks revealed evidence of acid diffusion on the pulpal side of the cemented dentine and significantly lower pH when cemented with glass-ionomer and zinc phosphate than with zinc polycarboxylates.

Conclusions This study demonstrated that glass-ionomer exhibited a lower setting pH than zinc phosphate and zinc polycarboxylate, and acid diffusions from glass-ionomer and zinc phosphate cements were observed when placed on 0.25-mm-thick dentine disks.

Keywords: bovine dentine, glass-ionomer cement, pH, remaining dentine thickness, zinc phosphate cement, zinc polycarboxylate cement.

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Introduction

Conventional luting cements are made of liquid and powder components, which are set by an acid–base interaction (Smith 1983). The pH of the initial mix is low and rises to a level approaching neutrality during the course of the setting reaction (Smith & Ruse 1986). A slow change in pH may cause pulpal sensitivity, especially in areas where the remaining dentine layer is thin or damaged (Smith & Ruse 1986, Sonoda *et al.* 2001, Costa *et al.* 2002). In a study using five different glass-ionomer cements, the authors speculated that it was the time during which the pH was below 3, which determined the extent of sensitivity experienced by some patients (Smith & Ruse 1986).

The acid dissolves the smear layer and peritubular dentine, thereby increasing the permeability of dentine (Pashley *et al.* 1983). The effect of luting cements on dentine demineralization (Shimada *et al.* 1999) and their acidity (Smith & Ruse 1986, Wasson & Nicholson 1993) have been studied. Observation of cemented dentine specimens using either scanning electron or confocal laser scanning microscopy revealed that acid-containing cements had self-etching properties, which removed the smear layer in various degrees (Abe *et al.* 1984,

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Shimada *et al.* 1999). On the other hand, research on the diffusion of hydrogen and hydroxyl ions through dentine using an electrode showed that hydrogen ions penetrated more slowly than hydroxyl ions as a result of the buffering of hydrogen ions by hydroxyapatite and other components of dentine (Wang & Hume 1988).

Previously, changes in pH during the setting of luting cements were studied using an electrode placed on the cements (Smith & Ruse 1986, Wasson & Nicholson 1993). However, studies on the acidity of dental cements have been limited to the measurement of pH changes during setting. For unset cement, pH changes were measured by placing an electrode on the surface of the mixed cement. However, for set cement, the cement specimen was dissolved, and the pH of the slurry was recorded using an electrode. Therefore, it has been difficult to follow changes in pH of the setting cement once the cement becomes stiff.

In the present study, a pH-imaging microscope (SCHEM-100; Horiba Ltd, Kyoto, Japan) was used to overcome this difficulty. Sample preparation for the SCHEM-100 does not require its destruction by dissolution. The pH analysis can be performed by a simplified process of placing flat solid samples on a semiconductor silicon sensor, which has photocurrent characteristics (Nomura *et al.* 1997, Kitasako *et al.* 2002). The pH value-analysing technique using the SCHEM-100 has recently been introduced into dentistry (Kitasako *et al.* 2002, Hiraishi *et al.* 2003) for the evaluation of carious dentine or chemical characterization of the dentine surface. Following the pH measurement of setting cement, each luting cement was set on a flat bovine dentine disk, and the pH change on the back surface of the cemented dentine was observed.

The aim of this study was to measure the change in pH of the surface of setting and stiff cements continuously during setting and to observe evidence of acid diffusion from the luting cements.

Materials and methods

A glass-ionomer, zinc phosphate and zinc polycarboxylate cement were used (Table 1). All materials were mixed under room conditions (24 ± 1 °C and 50 ± 5% relative humidity) according to the manufacturers' instructions.

Sample preparation

pH measurement of luting cements

A glass electrode pH meter (TWIN pH; Horiba Ltd, Kyoto, Japan) was used to measure the pH of the liquid component and each unset cement (immediately after mixing).

The SCHEM-100 was utilized to measure changes in pH of the luting cement. Each freshly mixed cement was placed on the sensor of the SCHEM-100. The pH-imaging sensor is based on a light-addressable potentiometric sensor (LAPS) made of Si_3N_4/SiO_2 and silicon (Si; Hafeman *et al.* 1988). For set-up of the pH-imaging sensor, a 1.5% agar solution, consisting of 0.1 M potassium chloride and agar powder, was used to make 1-mm-thick agar film on the semiconductor sensor. When the sample was placed on the agar film, H^+ or OH^- ions travelled from the dentine surface into the agar film. The AC photocurrent, which varied depending on the quantity of H^+ or OH^- ions coming from the sample through the agar film, was converted into grayscale pixels, and each pixel was arranged to the pH image using image analysis software (Image-Pro Plus; Media Cybernetics, MD, USA). The pH measurement was conducted at multiple points, and then the pH distribution was displayed as pH images. As the grayscale of each pixel that made up the image correlated with the pH value at each measurement, the pH value of each pH image could be examined using EXCEL software (Microsoft Corp., Redmond, WA, USA; Nakao *et al.* 1996). The spatial resolution and the pH resolution of the sensor were 300 μm and 0.1 pH, respectively.

Table 1 Materials used in the study

Material	Content (Batch No.)	Manufacturer
Fuji I (glass-ionomer cement)	P (030681): Fluoro-alminosilicate glass L (0102051): Acrylic-maleic acid copolymer, Polybasic carboxylic acid, water P/L ratio = 1.8 (g g^{-1})	GC Co., Tokyo, Japan
Elete 100 (zinc polycarboxylate cement)	P (0103161): Zinc oxide, magnesium oxide L (0103211): Phosphoric acid, aluminium, water P/L ratio = 1.45 (g mL^{-1})	GC Co., Tokyo, Japan
Hy-Bond Carbo (zinc polycarboxylate cement)	P (029181): Zinc oxide, HY-agent (tannic acid, SrF_2, ZnO, ZnF_2) L (039185): Tri-carbonic acid, acrylic acid copolymer, water, additives P/L ratio = 2.2 (g g^{-1})	Shofu Inc., Kyoto, Japan

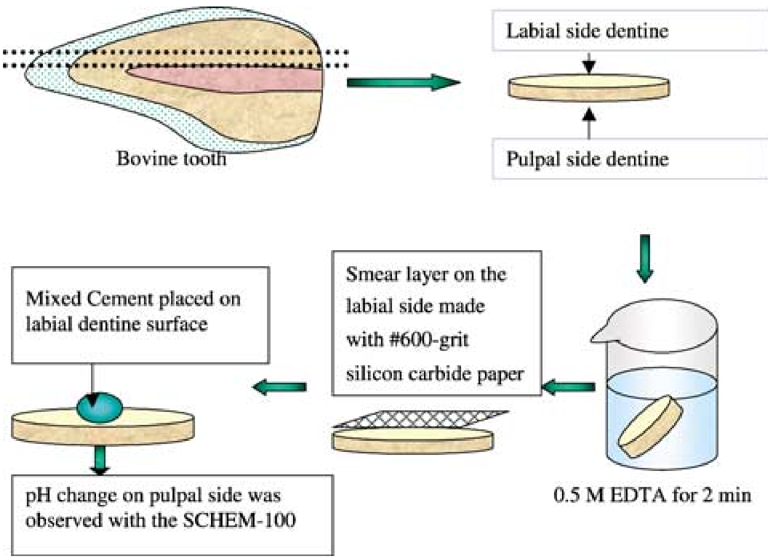

Figure 1 Bovine dentine sample preparation.

pH measurements were undertaken every 3 min for up to 30 min. After that time, the pH of the set cement was measured at given time intervals: 60 min, 90 min, 120 min, 1 day, 3 days, 1 week and 1 month. The set cements were stored in distilled water (pH 7.0 ± 0.2) after the first 30 min and between measurements. The pH measurements were made in triplicate.

pH measurement on bovine dentine surface on which a luting cement was placed

Forty-eight extracted bovine incisors, stored frozen for no longer than 1 month, were used. Their roots were sectioned at the cement–enamel junction with a high-speed diamond bur. The crown segments were sliced using a diamond saw (Leitz Instruments, Heidelberg, Germany) under water coolant in a similar manner as described by Tagami *et al.* (1989). The first section was through the labial dentine and the second made parallel to the first section through the pulp chamber, keeping the pulp wall intact (Fig. 1). The pulpal surfaces of the sliced disks were ground with 600-grit silicon carbide paper under running water until the pulpal walls were removed. The labial surfaces were ground in the same manner until disks approximately 0.55 and 0.30 mm thick were obtained. The dentine disks were treated with 0.5 M EDTA (pH 7.4) for 2 min to remove the smear layers on both the surfaces, which promoted dentine permeability through the dentinal tubules. Following this, the labial surfaces were ground again with 600-grit silicon carbide paper under running water to reduce the thickness and create smear layers only on the labial dentine surfaces as in the clinical situation. The disks were washed for 30 s in distilled water to remove chemical contaminants of the 0.5 M EDTA. Consequently, dentine disks were prepared with a smear layer on the labial surface and no smear layer on the pulpal surface. The disks were randomly divided into six groups of eight, with each group representing a different cement and thickness. The freshly mixed cement was placed on the labial surface of a dentine disk, giving a cemented dentine area of approximately 5 mm diameter in the centre of the disk (Fig. 1). The dentine disk was then placed, pulpal surface down, on the sensor of the SCHEM-100. The lowest pH value on the pulpal dentine surface under the setting cements was recorded every 3 min for 30 min.

Statistical analysis

The means and standard deviations were calculated for the pH values of the luting cements and the lowest pH value on the pulpal surfaces of cemented dentine disks. The data were analysed using repeated measure ANOVA and, where appropriate, one-way ANOVA and Fisher's Protected Least Significant Difference test with the value of significant set at the 5% level to determine any significant differences.

Results

pH value of luting cements

The pH of liquid component of glass-ionomer cement, zinc phosphate cement and zinc polycarboxylate cement was 1.1, 0.4 and 1.1, respectively (Fig. 2). Zinc phosphate

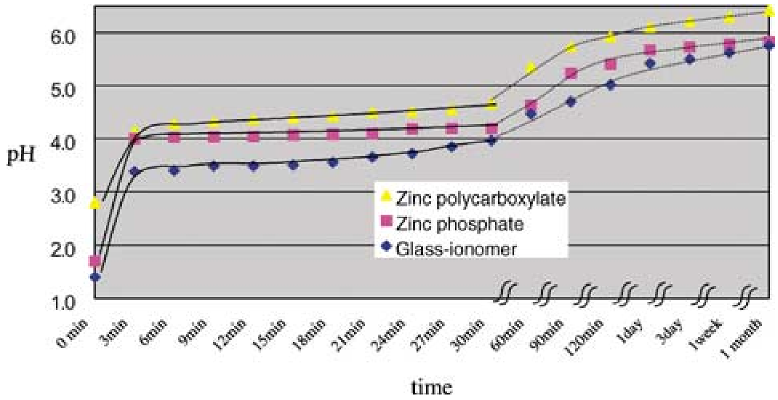

Figure 2 The change in pH value for the three luting cements as they set.

cement and zinc polycarboxylate cement reached pH 4.0 in 3 min after mixing. The pH of zinc phosphate cement increased rapidly, reaching pH 4.0 in 3 min, and glass-ionomer cement remained at less than pH 4.0 for 30 min after mixing. Repeated measure ANOVA revealed that the effects of luting cements and the effects of time were significant ($P = 0.0071$ and $P < 0.0001$, respectively), and the luting cements by time interaction were significant ($P = 0.0221$). Glass-ionomer cement showed significantly lower pH between 3 and 15 min than zinc phosphate cement and zinc polycarboxylate cement ($P < 0.05$). Over time, neutralization also proceeded furthest for zinc polycarboxylate cement, reaching pH 6.3 in 1 week. Although there was no significant difference between glass-ionomer cement and zinc phosphate cement at 18 min and thereafter, the increase in pH value in glass-ionomer cement was much slower, reaching pH 5.0 in 120 min and 5.8 in 1 month.

pH value on bovine dentine surface on which a luting cement was placed

Figure 3 shows representative pH images of the pulpal side of a 0.25-mm-thick dentine disk, on which each mixed cement was placed on the labial side. Regarding the TIFF images of glass-ionomer cement and zinc phosphate cement, the areas of low-intensity grayness were seen in the centre of pulpal dentine side relevant to the cemented area, indicating a reduction in pH value compared to normal dentine surrounding the cemented area. TIFF images of zinc polycarboxylate cement revealed little evidence of pH change on the pulpal surface. For all groups prepared in 0.50 mm thickness, no distinctive changes were observed in the TIFF images. Figure 4 shows the pH change on the pulpal side with each mixed cement on the labial side for 30 min. For all groups of 0.50 mm thickness, there were no significant

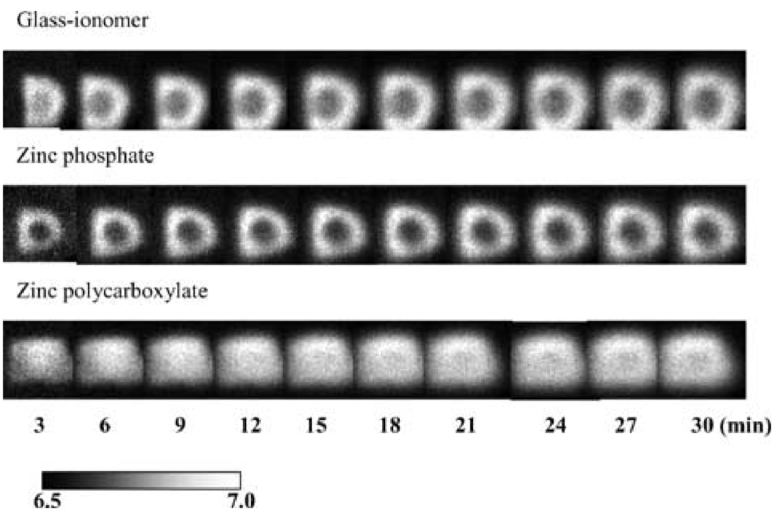

Figure 3 Representative pH images of the pulpal side over time after the mixed cements were set on the labial side of 0.25-mm-thick dentine disks. Images of glass-ionomer cement and zinc polycarboxylate cement show low-intensity grayness (a decrease in pH value) in the centre beneath the cemented area, whilst little evidence of pH change of zinc polycarboxylate cement group. Note: the horizontal bar shows the grayscale for pH value.

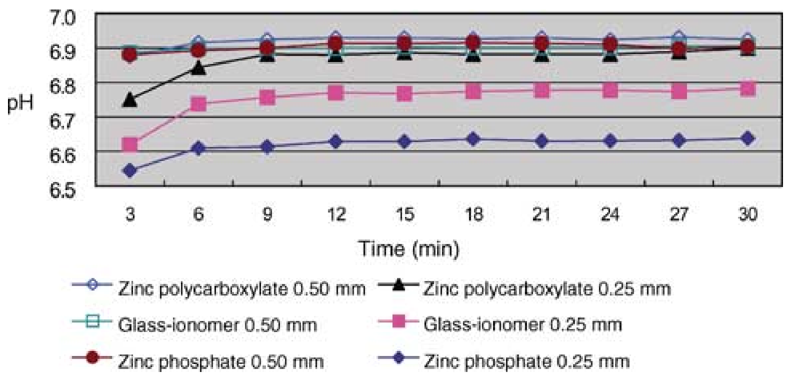

Figure 4 The change in pH value on the pulpal side with the mixed cements placed on the labial side for 30 min. One-way ANOVA and Fisher's PLSD test showed no significant difference amongst the three luting cements on 0.50 mm-thick bovine dentine and a significant difference on 0.25 mm-thick dentine at 6 min and thereafter.

differences between the cements for 30 min. For all groups of 0.25 mm thickness, the result of repeated measure ANOVA indicated that the effects of luting cement and time were significant ($P < 0.0001$), and the interaction between cements and time was not statistically significant ($P = 0.88$). For the three groups of 0.25 mm thickness, one-way ANOVA and Fisher's PLSD test revealed that whilst glass-ionomer cement and zinc phosphate cement showed no significant difference in pH value at 3 min, the pH value at 6 min and after was significantly different amongst the three cements.

Discussion

It has been important to measure the change in pH of luting cements because the high acidity of luting cements has been associated with pulp irritation and possible necrosis (Smith & Ruse 1986). For the difference between surface pH and internal pH, it indicated that the effect on the surrounding tissue of a cement might depend more on the extent to which the unneutralized acid on the surface could be released than on the extent of the reaction that the internal majority of the cement had undergone (Woolford 1989). With the SCHEM-100, it was possible to continuously measure the pH change on the surface of a luting cement during the course of the setting reaction over time throughout the experiment when a mixed cement or stiff cement was placed on the sensor.

In an early study on silicate cement, acids at pH 2.8–2.9 induced vascular thrombosis in the pulp of a rat, which indicated that a significant duration of acid exposure below this pH level on thin dentine or pulp might result in damage and, ultimately, in necrosis in the early stage of setting (Svare & Meyer 1965). Plant & Tyas suggested a possible critical cement pH of around pH 2.0 for 5 min for inducing a damaging pulp response (Plant & Tyas 1970). Smith & Ruse showed that the initial setting of some glass-ionomer cements were slow, with the pH being below 3 for 10 min, and suggested that this might be the cause of sensitivity in the case of these cements (Smith & Ruse 1986). This finding is similar to that of the present study, which showed a significantly slow rise in pH for glass-ionomer cement: the pH value immediately after mixing was 1.4 and reached 3.4 in 3 min. The main factor for the slow change in pH might be the aqueous solution of acrylic-maleic acid copolymer and polybasic carboxylic acid in glass-ionomer cement liquid (Shimada *et al.* 1999). Polybasic carboxylic acid includes a certain acid, which initially reacts with the glass filler and contributes to a longer period of low pH. This acid, an important additive that controls the setting of glass-ionomer systems, inhibits the initial acid–base reaction and allows the cement to maintain fluidity for an extended period, resulting in an extended working time and an accelerated setting reaction (Prosser *et al.* 1982).

On the other hand, the liquid in zinc phosphate cement and zinc polycarboxylate cement reacts rapidly with the zinc oxide powder during setting, resulting in a rapid rise in pH (Smith & Ruse 1986). In the present study, the pH of zinc phosphate cement and zinc polycarboxylate cement was found to be above 4.0 at 3 min after mixing.

On 0.25 mm-thick dentine slices, a pH change was observed on pulpal dentine surface beneath glass-ionomer cement or zinc phosphate cement, indicating that the acid induced from each cement had permeated the bovine dentine. The change in pH beneath zinc phosphate cement was significant compared with glass-ionomer cement and zinc polycarboxylate cement. For determining the factor of dentine permeability during setting, the chemical characteristics of cements, such as its low pH, low molecular weight of the acidic liquid

and its viscosity should be taken into consideration (Stanley 1990, Pashley 1992). Although the liquid and powder reacted rapidly, the acid from the zinc phosphate cement was able to penetrate into the dentinal tubules and pulp tissue because of its low molecular weight.

The permeability of bovine dentine was significantly less during the setting of glass-ionomer cement than during the setting of zinc phosphate cement despite the slow rise in pH of glass-ionomer cement after mixing. The acid in glass-ionomer cement possesses a higher molecular weight, limiting its diffusion through the dentinal tubules (Tobias *et al.* 1981).

For zinc polycarboxylate cement, the change in pH on the pulpal surface was not distinctive. This might be because of the rapid reaction between the powder and liquid, and the high molecular weight of the acidic liquid, which prevented the acid from zinc polycarboxylate cement being detected on the pulpal dentine surface.

The remaining dentine thickness (RDT) is one of the most important factors regulating the pulpal response (Costa *et al.* 2002). Dentine is contributive to reducing the potential for cytotoxicity of dental materials (Hume & Mount 1988). A previous study on the permeability of dentine has shown that when the thickness of the dentine decreases, its permeability increases (Pashley *et al.* 1989). This inverse relationship was explained by the increased diameter and number of the dentinal tubules close to the pulp tissue, and consequently higher dentinal permeability. Some studies have shown an inverse relationship between the RDT and the inflammatory pulp response (Hanks *et al.* 1988, Elbaum *et al.* 1992), demonstrating that a dentine thickness of 0.5 mm seemed enough to provide protection to pulp tissue against the diffusion of toxic substances. According to another histological finding, persistent inflammatory pulp response seemed to occur as a result of cytotoxic effects when the dental cavities had a RDT of less than 0.3 mm (Hebling *et al.* 1999).

Based on the results of the present study, 0.50 mm of dentine was able to prevent acidic penetration of glass-ionomer cement, zinc phosphate cement and zinc polycarboxylate cement; however, 0.25 mm of dentine was not able to do so when glass-ionomer cement or zinc phosphate cement was used. This finding is in agreement with the histological findings by Hanks *et al.* (1988) and Hebling *et al.* (1999). The pH value-analysing technique using the SCHEM-100 was able to measure the change in pH of setting luting cements over time, and to observe acid diffusion from luting cements through bovine dentine. Although this study failed to show direct effects of the acid or subsequent other toxic chemical diffusion, it was noteworthy that a RTD was evaluated by measuring pH change on pulpal surface for protection against acid diffusion by setting cements.

Conclusion

This study demonstrated that glass-ionomer cement exhibited a lower setting pH than zinc phosphate cement and zinc polycarboxylate cement, and the acid diffused through bovine dentine to the pulpal side when glass-ionomer and zinc phosphate cements were placed on 0.25 mm-thick dentine disks.

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